THE LIQUID DENSITY OF COMPLEX LIQUID MIXTURES

Keshavarz, Mohammad Hossein *
Department of Chemistry, Malek Ashtar University of Technology,
Zip code 83158, Isfahan, I.R. Iran.

Boushehri, Ali
Department of Chemistry, Shiraz University, Zip code 71454, Shiraz, I.R. Iran

ABSTRACT: *A second virial coefficient correlation suitable for two different temperatures ranges, $(T^*)^{-2} \leq 180$ and $(T^*)^{-2} > 180$, where T^* is $RT/\Delta H_{vap}$ is presented. The equation of state can be calculated for different, complicated non-polar, and slightly polar liquid mixtures at any temperature over the range from T_{tp} to T_c and up to high pressures. The latent heat of vaporization and density at the triple point are the only two parameters that are needed in these calculations. The results indicate that the liquid densities of liquid mixtures with quite different acentric factors can be predicted to within about 5%.*

KEY WORDS: *Compressed liquids and mixtures, Equation of state, Density, Second virial coefficients, Statistical mechanics.*

INTRODUCTION

We recall that a knowledge of the equation of state together with the specific heat constant is sufficient for determining all thermodynamic equilibrium properties. An analytical equation of state, recently obtained from statistical mechanics, can determine the P-V-T behavior of nonpolar and slightly polar molecules [1]. The linear empirical relation between the bulk modulus (reciprocal compressibility) and pressure at constant temperature, upon which many equations of state are based, can be derived from this new equation of state [2]. The three temperature-dependent parameters used in the equation are: the second virial coefficient B(T), the softness factor of the repulsion α(T), and the effective van der Waals covolume b(T) which is related to α by $b=\alpha+T(d\alpha/dT)$. One method for calculating these parameters makes use of the experimental heat of vaporization and the triple point density [3,4]. The enthalpy of vaporization and the liquid density at the triple point are related to the cohesive energy density of the regular solution theory [5]. In terms of these two scaling parameters (ΔH_{vap} , ρ_{tp}), the average contact pair distribution function has a single curve in $\lambda b\rho$ [3]. We saw that the liquid density of a compressed liquid mixture, using the equation of state with ΔH_{vap} and ρ_{tp} , can be determined to within about 5% when $(\Delta H_{vap}/RT)^2$ is less than or equal to 180 [4]. But the deviations become larger for the case of $(\Delta H_{vap}/RT)^2 > 180$ (large molecules in particular belong to this region). Thus a new correlation is

* *To whom correspondence should be addressed*
1021-9986/98/2/89 5/$/2.50

essential for this range of temperature.

In this paper, we introduce a new correlation which is valid over the temperature range $(T^*)^{-2}>180$, where T^* is $RT/\Delta H_{vap}$ (nearly up to freezing point). The equation of state with the new and previous correlations were tested on a large number of pure liquids and complex liquid mixtures with widely ranging acentric factors. The results show that one can obtain the liquid density at any temperature and up to high pressures (about 500 bar).

The equation of state and procedure

The statistical-mechanical theory, by the pressure equation, under the assumption of additive intermolecular potential [6], yields the following equation of state [7-9] which includes a small correction term, $[\delta b\rho^2(\alpha-B)]/(1+\delta b\rho)$, for the attractive force [1]

$$\frac{P}{\rho k_B T} = 1+ B\rho + \alpha\rho[G(b\rho)-1]+ \frac{\delta b\rho^2(\alpha-B)}{1+\delta b\rho} \quad (1)$$

where P is pressure, ρ is the number density, k_B is the Boltzmann constant, $G(b\rho)$ is an effective pair distribution function at contact for equivalent hard nonspherical convex bodies, and δ is a small constant. An accurate expression for G in the case of nonspherical convex bodies is given elsewhere[10]. We can obtain the Corresponding-States result by solving Eq. (1) for G and then treating G as a known function to be determined from experimental P-V-T data, which gives the surprisingly simple result, $G(b\rho) \approx (1 - \lambda b\rho)^{-1}$ [9]. In other words, a plot of G^{-1} against $b\rho$ is very nearly a straight line whose slope is $-\lambda$, and holds for any substance over the entire range of temperature and pressure. On substituting $(1-\lambda b\rho)^{-1}$ for G in Eq. (1), we obtain a general equation of state that is the starting point for the present work:

$$\frac{P}{\rho k_B T} = 1 + \frac{\rho(B-\alpha)}{1+\delta b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \quad (2)$$

It has been found that δ can be taken as equal to 0.22 λ for any complex fluid [1,11,12].

If the intermolecular potential is known, the three temperature-dependent parameters, $\alpha(T)$, b(T) and B(T), can be determined; such calculations have been carried out for a Lennard-Jones (12,6) potential and for an accurate noble gas potential, namely Ar-Ar potential [2]. In the absence of the knowledge of the intermolecular potential, we can assume some simple mean-spherical potential having two adjustable constants and adjusting these constants to fit B(T) in order to calculate $\alpha(T)$ and b(T) by numerical integration [1,7-9] or simply adjusting in terms of Boyle's constants rather than potential constants [9]. Since $\alpha(T)$ and b(T) are rather insensitive to the shape of the intermolecular potential, we can use another simple approach for finding them in terms of suitable reducing units such as the heat of vaporization (ΔH_{vap}) and the triple point density (ρ_{tp}) [3]. If a Lennard-Jones (12,6) potential is used, $\alpha(T)$ and b(T) are fitted by the expressions

$$\alpha\rho_{tp} = a_1\exp(-c_1T^*) + a_2\left\{1-\exp[-c_2(T^*)^{-1/4}]\right\} \quad (3)$$

$$b\rho_{tp} = a_1(1 - c_1T^*)\exp(-c_1T^*) + a_2\left\{1 - [1+(c_2/4)(T^*)^{-1/4}]\exp[-c_2(T^*)^{-1/4}]\right\} \quad (4)$$

where $a_1 = -0.1053$, $a_2 = 2.9359$, $c_1 = 5.7862$, and $c_2 = 0.7966$.

In our previous work [3,4], based on the experimental second virial coefficient of nonpolar and slightly polar molecules and two scaling factors (ΔH_{vap} , ρ_{tp}), we obtained the following correlation in the temperature range $0\le(T^*)^{-2}\le180$

$$B\rho_{tp} = 0.4038908 - 0.0764845(T^*)^{-2} - 0.0002504(T^*)^{-4} \quad (5)$$

The Eqs. (2)-(5) and the value of λ are sufficient to determine the P-V-T surface of nonpolar fluids with a low percent error at the temperature range $0\le(T^*)^{-2}\le180$.

A new correlation

We need a new correlation which can predict the dimensionless second virial coefficient ($B\rho_{tp}$) over the temperature range $(T^*)^{-2}>180$. One of the methods which provides a good correlation for the second virial coefficients of normal fluids is the Pitzer-Curl-Tsonopoulos correlation [13]; the necessary input information for this correlation are the critical temperature, the critical pressure, and the Pitzer acentric factor. We used the Pitzer-Curl-Tsonopoulos correlation and found the following correlation which holds very well over the temperature range $(T^*)^{-2}>$ 180 for nonpolar and slightly polar compounds.

Table 1: The used parameters for different compounds

Substance	$\Delta H_{vap}/R$ (K)	ρ_{tp} (mol lit^{-1})	T_{tp} (K)	λ $(T^*)^{-2} \leq 180$	λ $(T^*)^{-2} > 180$
SO_2	2947	22.71	197.9	0.414	0.457
CF_2Cl_2	2438	14.91	118.2	0.475	0.472
$CFCl_2H$	2970	16.54	138.2	0.486	0.468
$C_2F_3Cl_3$	3382	9.098	236.6	0.454	0.439
n-C_4H_{10}	2875	12.65	134.9	0.491	0.472
n-C_5H_{12}	3470	10.55	143.5	0.515	0.485
n-C_6H_{14}	3628	8.781	177.8	0.497	0.469
n-C_7H_{16}	4039	7.720	182.6	0.513	0.479
n-C_8H_{18}	4356	6.753	216.4	0.514	0.484
iso-Octane	3808	6.950	165.8	0.504	0.479
n-C_9H_{20}	4594	6.037	219.7	0.518	0.476
n-$C_{10}H_{22}$	4923	5.393	243.5	0.519	0.477
n-$C_{11}H_{24}$	5312	4.965	247.6	0.537	0.487
n-$C_{12}H_{26}$	5607	4.522	263.6	0.540	0.487
n-$C_{13}H_{28}$	6134	4.200	267.8	0.559	0.502
n-$C_{14}H_{30}$	6432	3.900	279.0	0.567	0.506
n-$C_{15}H_{32}$	6764	3.650	283.1	0.576	0.513
n-$C_{16}H_{34}$	7112	3.419	292.0	0.583	0.523
n-$C_{17}H_{36}$	7285	3.229	295.2	0.589	0.524
n-$C_{18}H_{38}$	7564	3.051	301.4	0.600	0.531
Propene	2232	18.33	87.90	0.468	0.460
1-Butene	3178	14.21	87.80	0.540	0.511
1-Pentene	3080	11.65	107.9	0.503	0.487
Propyne	2672	18.93	170.5	0.460	0.444
Toluene	4283	10.44	178.2	0.508	0.480
o-Xylene	4478	8.663	248.0	0.485	0.461

$$B\rho_{tp} = -65.17974 + 0.461088(T^*)^{-2} - 0.00121238(T^*)^{-4} \quad (6)$$

Two values of λ can be obtained from Eq. (1) by fitting the ρ_{tp} and ΔH_{vap} data which depend on the temperature range. The λ values for some compounds are given in Table 1.

Extension to mixtures

The equation of state (Eq.(2)) can be extended to mixtures of any number of components in the following form

$$\frac{p}{\rho k_B T} = 1 + \rho \sum_{ij} x_i x_j (B_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij} \quad (7)$$

where x_i and x_j are mole fractions; for a single substance $F_{ii}^{-1} = 1 + 0.22\lambda b\rho$ and $G_{ii}^{-1} = 1 - \lambda b\rho$. The quantities G_{ij} and F_{ij} for mixtures are given elsewhere [14]. Since $\Delta H_{vap} \sim \varepsilon$ and $\rho_{tp} \sim r_m^{-3}$, the simplest combining rules are a geometric mean for ΔH_{vap} and an artithmetic mean for ρ_{tp} which can be used to predict the unlike-molecule interactions from the like-molecule interactions. Thus the combining rules will be

$$(\Delta H_{vap})_{ij} = [(\Delta H_{vap})_i(\Delta H_{vap})_j]^{1/2} \quad (8)$$

$$(\rho_{tp})^{-1/3}_{ij} = 0.5[(\rho_{tp})^{-1/3}_{i}+(\rho_{tp})^{-1/3}_{j}] \quad (9)$$

In order to predict the values of α_{ij}, b_{ij} and B_{ij} the resulting $(\Delta H_{vap})_{ij}$ and $(\rho_{tp})_{ij}$ were used in Eqs. (3)-(6) as for pure substances.

We have tested the present prediction scheme for compressed liquid mixtures having a variety of structural types. Our survey fluids can be classified into the following groups:

1. Noble gases
2. Diatomics
3. Inorganic polyatomics (e.g. SO_2)
4. Alkanes up to octadecane
5. Simple alkenes (e.g. propene)
6. Simple alkynes (e.g. propyne)
7. Simple aromatic hydrocarbons (e.g. toluene)

Compressed liquid mixtures of the above groups have been tested at different temperatures and compositions. The results show that the density of liquid mixtures can be predicted with high accuracy. These are shown for some equimolar binary mixtures in Figs. 1-3.

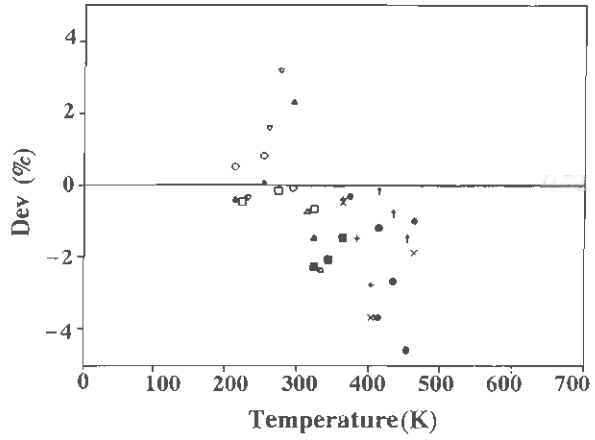

Fig. 1: Deviation plot for the volumetric behavior of equimolar binary liquid mixtures vs. temperature at 10 bar, with $Dev\% = (V_{cal}-V_{COSTALD})/V_{COSTALD}$. *The* V_{cal} *is the molar volume* (cm^3/mol) *of the present calculations and* $V_{COSTALD}$ *is the molar volume determined by the Corresponding States Liquid Density [17]. The points are:* ∇ $C_3H_8+CF_2Cl_2$; ■ *propene+n-*C_4H_{10}; ▲ *propyne+*CF_2Cl_2; ○ *propyne+1-butene;* □ *1-butene+n-*C_4H_{10}; Δ *n-*C_5H_{12}*+n-*C_9H_{20}; + *n-*C_6H_{14}*+n-*$C_{13}H_{28}$; × *n-*C_7H_{16}*+n-*$C_{12}H_{26}$; † *toluene+n-*C_8H_{18}; ◆ *n-*C_8H_{18}*+n-*$C_{12}H_{26}$; ⊕ *n-*C_8H_{18}*+n-*$C_{14}H_{30}$.

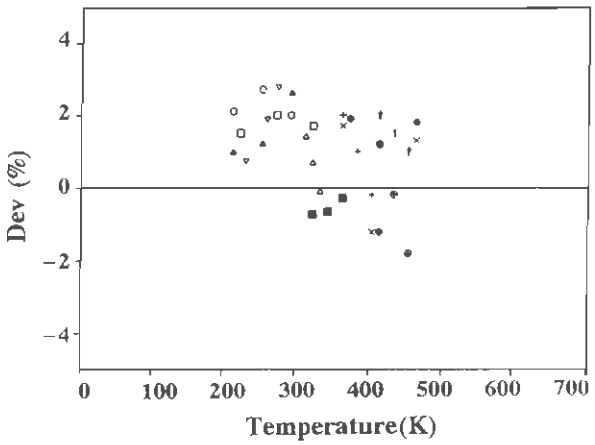

Fig. 2: Deviation plot for the volumetric behavior of equimolar binary liquid mixtures vs. temperature at 200 bar. The parameters and points are defined as in Fig. 1.

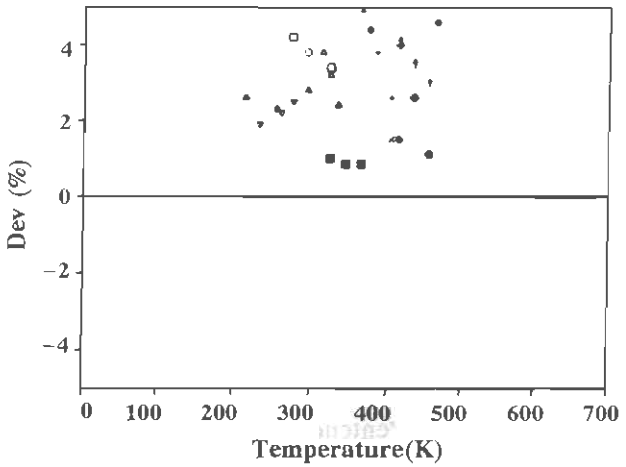

Fig. 3: Deviation plot for the volumetric behavior of equimolar binary liquid mixtures vs. temperature at 500 bar. The parameters and points are defined as in Fig. 1.

In brief, the values of enthalpy of vaporization can be obtained by the Clausius-Clapyron equation from the various vapor pressure measurements [15]. For most common liquids, liquid specific volumes are relatively easy to measure experimentally or calculate with high accuracy from a suitable estimation method [16]. Once ΔH_{vap} and ρ_{tp} are known, we can obtain α_{ij}, b_{ij} and B_{ij} for any pure liquid or complex liquid mixture. From Eqs. (3)-(6), three temperature-dependent parameters, α_{ij}, b_{ij} and B_{ij} are sufficient for the determination of the equation of state for any real molecular fluid.

RESULTS AND DISCUSSION

Since B(T) the second virial coefficient of the vapor would not be known experimentally for many compounds of interest, the present method can be used for liquid mixtures with reasonable accuracy only by knowing two parameters, ΔH_{vap} and ρ_{tp} . This is an advantage over the previous statistical-mechanical methods which would need ε and r_m from experimental values of B(T). In addition, we can predict the three parameters α(T), b(T) and B(T) with satisfactory accuracy from a knowledge of ΔH_{vap} and ρ_{tp}, , without knowing any details of the intermolecular potential. The P-V-T behavior of a mixture can be calculated from Eq. (7) by using Eqs. (3)-(6) in conjunction with Eqs. (8) and (9); the deviation plots for some equimolar binary mixtures are shown in Figs. 1-3.

The average contact pair distribution function can be calculated with a knowledge of ΔH_{vap} and ρ_{tp} by which the linear dependence of G^{-1} on $\lambda b\rho$ for any liquid is given a strong basis in statistical mechanics [3]. Although the theory gives no explanation as to why a plot of G^{-1} vs. $\lambda b\rho$ is a straight line, it indicates that G is a function of a single variable $b\rho$ for a pure substance.

Received, 4th November 1995 ; Accepted, 27th July 1998

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